

XVIII. Experiments on the Effect of various Substances in lowering the Point of Congelation in Water. By Charles Blagden, *M. D. Sec. R. S. and F. A. S.*

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THE experiments which were necessary, in order to determine what effect the admixture of various substances would produce upon the property of water to be cooled below the freezing point*, naturally led me to a more particular consideration of the power of such admixtures in making water require a greater degree of cold before it congeals. Many curious questions occurred on this subject, which could only be answered by fresh experiments. These were made nearly in the same manner as the preceding; that is, the liquor, whose freezing point I meant to try, was put into a glass tumbler, to the height of two or three inches above the bottom, and the tumbler was then immersed in a frigorific mixture of common salt and ice or snow. As the object was seldom to cool the liquor as much as possible below its freezing point, the operation required no particular care, but the frigorific mixture was commonly permitted to act with its full force: wherefore, some parts of the liquor were often much colder than others; and particularly, near the top, a thermometer would usually stand several degrees higher than toward the bottom, because the surface was constantly warmed by the air of the room.

* See p. 125. of this Volume.

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My first object of investigation was the ratio according to which equal additions of the same substance depress the freezing point. I began with common salt; and in order to avoid as much as possible a fallacy in the experiments, because the ordinary salt is never pure, and often not perfectly neutral, I chose some clean salt, in fair crystals, which is sold in London under the name of Borrowstounness pure salt. This salt I dissolved in distilled water, in various proportions, and found the corresponding points of congelation to be as is expressed in the annexed table; where the first column indicates the number of parts and decimals of water to one part of the salt, and the second column shews the freezing point found by the experiment. It appeared clearly, on comparing the proportions of water to salt, with the corresponding number of degrees which the freezing point was reduced below 32° , that the effect of the salt was nearly in a simple ratio; namely, that if the addition of a *tenth* part of salt to the water sunk the freezing point about 11 degrees, or to 21° , it would be depressed double that quantity, or to 10° nearly, when a *fifth* part of salt was dissolved in the water. To shew, therefore, how far this simple proportion is exact, I have added a third column to the table, which is made by selecting the lowest freezing point that was obtained without ambiguity in the experiment, and calculating, by a simple inverse proportion, what all the other points should have been according to that ratio. Thus when a fourth part of its weight of common salt was dissolved in water, I found the freezing point of the liquor to be 4° ; therefore, to determine what it should be when only $\frac{1}{32}$ part of salt was added to the water, the formula is $32 : 4 :: 28$ (the number of degrees that the point 4° is below the freezing point of pure water) : $3\frac{1}{2}$; which subtracted from 32° gives

$28\frac{1}{2}$

$28\frac{1}{2}$ for the freezing point of that solution. All the rest of the third column of the table is found in the same manner, and with very little trouble, because $4 \times 28 = 112$ is a constant number, which being divided by the numbers of the first column, the quotient is the number of degrees sought. In all the experiments, none but distilled water was employed.

Common Salt.

Proportion of water to the salt.	Freezing point by the experiment.	Freezing point by cal- culation.	
32 : 1	29°	28 $\frac{1}{2}$	The third column is calculated from the last experiment, in which the freezing point of a solution of one part of salt in four of water proved to be +4°.
32 : 1	28 +	28 $\frac{1}{2}$	
24 : 1	27 $\frac{1}{2}$	27 $\frac{1}{3}$	
16 : 1	25 $\frac{1}{4}$	25	
10 : 1	21 $\frac{1}{2}$	20 $\frac{3}{4}$	
7,8 : 1	18 $\frac{1}{2}$	17 $\frac{2}{3}$	
6,2 : 1	13 $\frac{1}{2}$	14	
5 : 1	9 $\frac{1}{2}$	9 $\frac{1}{2}$	
5,5 : 1	7 $\frac{1}{5}$	7	
4 : 1	4	4	

The numbers in the third column of the table come so near to those in the second, that most likely the small differences between them ought to be ascribed to errors in the experiment; whence we should conclude, that the salt lowers the freezing point in the simple inverse ratio of the proportion which the water bears to it in the solution.

In the course of the experiments made with the different solutions of this salt, some phenomena occurred which deserve further attention.

1. This solution was in one instance cooled $8\frac{1}{2}$, and in several 5 or 6 degrees, below its freezing point; but in general it

shot rather more readily than some other solutions; which I ascribed, from the analogy of my former experiments, to its less transparency. Though the common salt did not form a turbid solution, yet there was something of a greyish cast, much like what is produced by the mixture of a small portion of clay with pure water; and the caution in conducting the operation, necessary to make solutions of this salt cool a certain number of degrees below their freezing point, seemed to be nearly the same as would be required with water equally tinged by means of clay.

2. When the solution was very strong, nearly saturated with the salt, cooling it tended somewhat to lessen this greyish cast, to render it rather more limpid: as was particularly the case in a saturated solution which I cooled to 0° . I suspect this effect takes place when the solution begins to expand with the cold.

3. In the strong solutions, when the proportion of salt was as much as one-fifth, before the real congelation came on which reduced the whole to one temperature, several small stellated crystals formed in the liquor, which increased very slowly. These were real ice of the salt water; but the cold being in this case very little below the freezing point of the solution, there was little power to make them spread; and sometimes, when this occurred, I believe, part of the solution toward the top was rather above than below the freezing point. Similar phænomena were observed, and in a still more remarkable manner, in the solutions of some other salts, always when they were very strong: and it may be given as a general fact, that in solutions approaching to saturation, though the formation of one glacial crystal does, as in pure water, tend to make the whole freeze and come up to an uniform temperature, yet the shooting goes on much more slowly, as if the

salt opposed some resistance, or at least proved an impediment, to the progress of the crystallization. By stirring the solution, however, when these stellated crystals once began to form, they quickly increased in bulk, or became more numerous, and the liquor assumed its freezing temperature.

4. This salt with snow, in the manner of frigorific mixtures, produced a cold of -4° .

The next salt which I tried for its effect in lowering the freezing point of water, was nitre. It was part of a large compound crystal, or bundle of crystals, apparently very pure, such as is used in manufacturing the best gunpowder. This being mixed with the distilled water, in different proportions, the solutions froze according to the following table.

Nitre.

Proportion of water to the salt.	Freezing point by the experiment.	Freezing point by calculation.
32 : 1	$30\frac{1}{2}$	$30\frac{1}{2}$
24 : 1	30	30
16 : 1	$28\frac{3}{4}$	29
10 : 1	27	$27\frac{1}{4}$
8 : 1	26	26
7,9 : 1	$26\frac{1}{2}$	salt deposited
7 : 1	$26\frac{1}{2}$	salt deposited
6,85 : 1	27	{ much salt deposited.

The third column is calculated from the fifth experiment, in which the freezing point of a solution of one part of salt in eight of water proved to be 26° .

Nitre is well known to differ from common salt in being much more soluble in warm than in cold water. Hence it would be nothing remarkable, that the solutions being made in water

water above the freezing point, some of the salt should, when they exceeded a certain strength, be deposited before they began to freeze. But a further question occurred here, whether, when a solution was cooled below its freezing point, the salt would still continue to be deposited; or whether it would not have parted with all the salt it was obliged to let go by the time it came to the degree at which it was to freeze, and would retain the remainder notwithstanding any subsequent cooling. To determine this, I noticed carefully the quantities of salt deposited at the bottom of the tumbler, in comparison with the cold of the solution as shewn by the immersed thermometer; and I found, that in some cases (for instance, when the salt was to the water only as 1 : 10) the deposition did not begin till after the solution had passed its freezing point; and that, when it began earlier, still there was no stop at the freezing point, but the quantity continued augmenting as the cold of the solution proceeded, and, as far as I could judge, rather in an increasing ratio. Thus when the saturated solution was cooled 8 or 10 degrees below its freezing point, which often happened, the collection of nitre at the bottom was very great; and in this manner I could render a saturated solution of nitre no longer saturated when it came to freeze, the deficiency being sometimes so great as to raise the point of conge-
lation a degree or more. Hence was ascertained the unex-
pected fact, that the lower such solutions are cooled, the higher is their freezing point.

The nitre deposited by the solution as it cooled, formed, if the vessel remained at rest, small but very white and compact prismatic or needle-like crystals, of considerable length, pointing different ways, and at last curiously interwoven with one another. But if these were broken down, or the solution was stirred

stirred with any force, the remaining nitre deposited itself in such minute crystals as to have much the appearance of a powder; I suppose from the destruction of the regular surfaces upon which it would otherwise have continued to form.

Frequently, in the stronger solutions, there appeared near the bottom and side of the tumbler many elegant stellated crystals, perhaps a quarter of an inch in diameter, all separate, but sometimes crowding very close upon one another, so as to exhibit a spectacle of much beauty.

The ice of solutions of nitre, especially when it began to thaw, was very different from common ice, having a soft woolly appearance, as if of a more tender and loose texture. Something of the same kind was observable in the ice of all the other solutions, sufficiently distinguishing it from any that can be formed of pure water.

All the solutions of nitre were remarkably limpid, having no tendency to an opaque or turbid cast; and accordingly they were very easily cooled below the freezing point, and could not but with difficulty be made to shoot till they had passed it many degrees. In two instances they cooled more than 10 degrees; namely, a solution of one part of nitre in 24 of water cooled slowly to $19^{\circ}\frac{1}{2}$, and then shooting, the thermometer came up to 30° ; and another solution, in which the nitre was to the water as 1 : 10, cooled rather below 16° , and having produced some stellated crystals, rose, when the perfect congelation took place, up to 27° .

As, when pure water is cooled below its freezing point, the least particle of ice or snow brought into contact with it causes an instant congelation, I was curious to know whether the same effect would be produced when salts were dissolved in the water. Therefore, having one of these nitrous solutions, whose

proportions were 8 : 1, I cooled it to 24° , about two degrees below its freezing point, and then, no salt being deposited, I put into it a small bit of ice. The effect of this was not instantaneous, as in pure water, though ultimately the same; the bit of ice gradually enlarged, and when it was stirred about in the liquor, a number of star-like crystals formed, which being scattered through it soon brought it to an uniform temperature of 26° . This same solution, when cooled in a preceding experiment to 18° , had its freezing point at 27° , from the quantity of nitre that had been deposited. In all solutions, therefore, of such salts as are much more soluble in hot than in cold water, if it be desired to find their freezing point when they are loaded with as much of the salt as the water can contain at that temperature, the most effectual method is to oblige them to shoot, as soon as they can be made to do so, by putting in a small bit of ice or snow; for thus the fallacy which might otherwise arise from the deposition of some of the salt will be avoided.

A doubt having been suggested, whether the contact of a crystal of salt might not also bring on the congelation, that experiment was tried, but it produced no effect. Indeed, the formation of saline crystals in these experiments, the liquor still remaining fluid, was a sufficient proof to the contrary.

There is another phaenomenon which I thought took place in solutions of nitre and some other salts, but could not absolutely satisfy myself concerning it; namely, that the deposition of some salt hastened that of the remainder. For instance, suppose that a solution of nitre in the proportion of 1 : 8, would retain the whole of its salt at its freezing point of 26° ; then, if another solution were made much stronger, it would begin to deposit its salt before it came to 26° ; and when cooled to

26°, it would not have just lost the difference between the proportions of 6 : 1 and 8 : 1, but would have deposited more of the salt, so that now at 26° it would contain perhaps only a tenth of nitre; as if the formation or existence of some crystals in the solution facilitated the separation of the salt, or constituted an attractive power counteracting the attraction of the salt to the water. It would have required a particular series of experiments to ascertain this as a fact; but several observations incline me to believe it is so; and the consequences to be drawn from it would be sufficiently curious, and applicable to many points of theory. Of the same nature, perhaps, is another circumstance already hinted at, that after the solution has begun to form crystals of nitre, the deposition proceeds with increased rapidity as the cooling goes on. This may, indeed, be owing to the attraction of the water to the salt decreasing in a progressive ratio with each degree of cold; but it may also depend on the attracting surfaces being multiplied as more crystals are formed: and stirring the liquor seems to hasten the progress of the deposition; which may be ascribed to its bringing fresh portions of the solution perpetually to those attracting surfaces; for, if there be such an attraction, it can scarcely be supposed to take place at any sensible distance.

Upon the whole it seems evident from the preceding table, that the effect of nitre, like that of common salt, is to depress the freezing point in the simple ratio of its proportion to the water; which will be found universally true when allowance is made for the deposition and other sources of fallacy already enumerated.

This nitre produced, with snow, a cold of between 26° and 27°.

As nitre funk the freezing point of water so little, namely, but 6 degrees, I had recourse for the next set of experiments to that neutral salt which, after sea salt, produces the greatest cold with ice; which is, the common sal ammoniac. The different solutions of this salt in water, being submitted to the action of the frigorific mixtures, froze according to the following table.

Sal ammoniac.

Proportion of water to the salt.	Freezing point by the experiment.	Freezing point by calculation.	
15,7 : 1	24 $\frac{1}{2}$	24 $\frac{1}{2}$	The third column is calculated from the last experiment but one, in which the freezing point of a solution of one part of the sal ammoniac in five of water proved to be 8°.
10 : 1	20 $\frac{1}{2}$	20	
9,8 : 1	20	19 $\frac{3}{4}$	
7,9 : 1	16 $\frac{1}{2}$	16 $\frac{3}{4}$	
6 : 1	12	12	
5 : 1	8	8	
4 : 1	4	salt deposited	

In this table also the numbers of the third colum agree sufficiently with those of the second to shew, that sal ammoniac, like the two preceding salts, depresses the freezing point in the simple ratio of the proportion in which it is mixed with the water.

The following is the account, as written at the time, of the experiment where the salt was to the water as 1 : 5. " This solution cooled down to 2° at bottom, but the frigorific mixture being insufficient, the top remained at 10°. The tumbler was then taken out, and the frigorific mixture being refreshed by stirring and the addition of new materials, it

" was

“ was replaced, when ice soon began to form at the bottom, “ like feathered crystals, which however shot out very slowly. “ But upon stirring the solution, a vast number of stellated “ feathered crystals presently formed in it, the thermometer “ rose immediately to $7^{\circ}\frac{1}{2}$, and was soon got to 8° .” I have transcribed these remarks, not only because they elucidate some of the phænomena mentioned in former experiments, but likewise on account of the striking analogy the crystals bore to the configurations observed in a drop of the solution of this salt viewed with the microscope. As the drop dries, great numbers of feathered crystals shoot out from its edges, and some more perfect stellated crystals are often formed in the middle; of which a pretty exact representation may be seen in BAKER’s Employment for the Microscope (p. 110. Pl. II.). The resemblance of both kinds of crystals, in these two different situations, is very great; and their particular figure is probably due to the same cause, a confused and constrained crystallization, occasioned in the one case by the hasty evaporation and want of room in the drop, and in the other case by the watery congelation acting upon and embarrassing the natural tendency of the salt.

A stronger solution of sal ammoniac, the proportions being 1 : 4, exhibited a still more beautiful appearance; for, beside the feathered crystals at bottom, and the stars floating in the middle, a third sort of crystals, most resembling the stars, attached themselves to the sides of the tumbler, and were seen through the glass as composing a great variety of brilliant *facettes*. In this experiment the solution was reduced below 1° , before any congelation began to take place, and a certain quantity of the salt fell to the bottom in the form of a white powder, about as much as reduced the liquor to the state of a
saturated

saturated solution at the freezing point, which therefore, when the congelation took place, proved to be 4° , instead of 2° , the number that would have answered to this proportion of salt.

It has been a question much contested, whether saline solutions deposit their salt upon freezing. That some separation, or a tendency to separation, takes place, many facts concur to prove; and among the rest some phænomena observed in the above-mentioned experiments. For instance, the stellated crystals, when first formed, were barely suspended in the water, and sometimes they even gradually subsided to the bottom; which shews, that they consisted of salt chiefly, only inviscated with ice, or at least of an over-proportion of salt: for the principal mass of ice formed in a saturated solution floats in it like common ice in pure water. Besides, it was almost constantly found, that when a crust of ice, which had been formed in a saline solution, began to thaw, a thermometer thrust into it rose somewhat higher than the point at which it had become stationary when the congelation took place; an indication that a less proportion of salt was present in it than had been in the whole solution. And if, after any solution had shot and formed a quantity of ice, the tumbler were still kept in the frigorific mixture, the thermometer immersed in the liquor gradually sunk lower and lower, as the congelation proceeded. But these very observations shew, that the separation is far from perfect; as the rise of the thermometer in the former case, or its descent in the latter, never exceeded one or two degrees, under a great variation in the quantity of ice in the solution.

Sometimes in solutions of sal ammoniac, and such other salts as separate by the cooling of the water, a sort of flocculent substance is formed, which subsides in the water, and thereby

thereby is distinguished from the proper ice of the solution, which it otherwise much resembles in appearance. It is composed principally of the deposited salt, in very minute crystals like powder, inviscated and kept together with a little ice.

Though sal ammoniac forms a tolerably transparent solution, yet I perceive that in these experiments it was in few instances cooled much below its freezing point; the most was nine degrees. I believe this to have been accidental, from no particular attention being now bestowed on that object.

The sal ammoniac, mixed with snow, produced a cold of from 4° to $4^{\circ}\frac{1}{2}$ of FAHRENHEIT's scale.

Of all the solutions submitted to these experiments, there were none more transparent and elegant than those made with Rochelle salt. The water dissolved a large proportion of this substance, and had its freezing point sunk according to the following table.

Rochelle salt.

Proportion of water to the salt.	Freezing point by the experiments.	Freezing point by calculation.	
10 : 1	$29\frac{1}{2}$	$29\frac{3}{4}$	The third column is calculated from the last experiment but one, in which the freezing point of a solution of one part of the Rochelle salt in two parts of water proved to be 21° .
5 : 1	$27\frac{1}{2}$	$27\frac{1}{2}$	
4 : 1	$26\frac{1}{3}$	$26\frac{1}{2}$	
2,6 : 1	24	$23\frac{1}{2}$	
2,25 : 1	$22\frac{1}{2}$	$22\frac{1}{4}$	
2 : 1	21	21	
1,6 : 1	24	salt deposited	

All the solutions of Rochelle salt bore to be cooled remarkably well. In one instance the liquor sunk $11\frac{1}{2}$ degrees below its

its freezing point; namely, the solution of one part of the salt in five of water, whose freezing point proved $27\frac{1}{2}$, and which cooled to 16° before the crystals of ice shot. In two other instances it sunk fully nine degrees below its freezing point. And, as already has been mentioned, the solutions of this salt are remarkably transparent.

In trying the greatest cold to be obtained by mixing Rochelle salt with snow, I could get the thermometer no lower than 24° .

GLAUBER's salt likewise was subjected to the experiments, but its utmost effect in producing cold with snow appearing to be only two degrees, this was too small a scale for settling any thing as to the ratio. A solution of it in water, in the proportion of $1 : 5$, cooled readily to 31° ; but the salt was deposited in great quantities, and often so fast, as to stop the cooling of the bottom of the liquor entirely, though the vessel was immersed in a strong frigorific mixture. This phænomenon has been observed before; but does not take place, to the same degree, in the solutions of any other salt with which I am acquainted, though I evidently perceived something of it in the strong solutions both of nitre and of sal ammoniac. It is exactly the converse of the cold produced by dissolving salts in water; for as there some heat is absorbed, and becomes latent, by the change of the salt from a solid to a fluid state, so here some heat is evolved as the salt assumes the solid crystalline form. The effect is so much more manifest with GLAUBER's salt only, I imagine, because the formation of the crystals proceeds so rapidly; whence the quantity of heat generated equals or exceeds the cold communicated by the freezing mixture. Some odd appearances are produced by this sudden

stop

stop of the cooling, and the rapid deposition of salt; for instance, a particular ebullition in certain parts of the liquor; but any intelligible description of them would be too minute.

These were all the salts with an alkaline basis which I tried. They all agreed as to the chief object of these experiments, namely, to determine how much the freezing point of water would be sunk by dissolving them in it in various proportions; which by these experiments appears to be, as nearly as could be determined, according to the simple ratio of the proportion each salt bears to the water.

I now resolved to try a few salts with an earthy and metallic basis.

The common *sal catharticus amarus* of the shops was the specimen I used of an earthy salt. It formed a turbid inelegant solution, as if dirty; and with various proportions of water produced the following points of congelation.

Sal catharticus amarus.

Proportion of water to the salt.	Freezing point by the experiment.	Freezing point by calculation.	
16 : 1	31°	31°	The third column is calculated from the last experiment, where the freezing point of a solution of one part of the <i>sal catharticus amarus</i> in 2,4 of water proved to be 25° $\frac{1}{2}$.
10 : 1	30°	30° $\frac{1}{2}$	
4 : 1	28 $\frac{1}{4}$	28°	
3 : 1	26 $\frac{4}{5}$	26 $\frac{4}{5}$	
2,4 : 1	25 $\frac{1}{2}$	25 $\frac{1}{2}$	

No salt was deposited from the strongest of these solutions; and as that which I used was a deliquescent salt, it must probably have been in a vast proportion to the water, before any

such effect would have taken place. I have sunk a thermometer with it and snow to $7^{\circ}\frac{1}{2}$; which, according to the proportions in the table, would make more than three parts of the salt to two of water. Accordingly, a large quantity of the salt was required to the snow.

No particular phænomenon was observed with this salt, except the singular configuration of its ice, which assumed the form of fungi, or of some kinds of lichen, with feathered striæ. The solutions were difficult to cool much below their freezing point.

Of the salts with a metallic basis, green vitriol affords one of the most transparent solutions in water. It sinks the thermometer nearly to $27^{\circ}\frac{1}{2}$ with snow, and reduced the freezing point of water according to the following table.

Green vitriol.

Proportion of water to the salt.	Freezing point by the experiment.	Freezing point by calculation.	
10 : 1	$30\frac{3}{4}$ °	31 °	The third column is calculated from the last experiment, in which the freezing point of a solution of one part of the green vitriol in 2,4 of water proved to be 28° .
6 : 1	$30\frac{1}{4}$	$30\frac{1}{2}$	
4 : 1	$29\frac{3}{4}$	$29\frac{1}{2}$	
3 : 1	$28\frac{3}{4}$	$28\frac{1}{4}$	
2,4 : 1	28	28	

The ice formed by these solutions assumed a foliaceous configuration, with a texture of penniform striæ, in some respects like the appearance exhibited by a drop evaporating under a microscope, as delineated by BAKER. Scarcely any salt gave the point of congelation so regularly in the proportion of the quantities mixed with the water, and none afforded solutions

which cooled more easily and readily below the freezing point. In two instances the cooling was more than 11 degrees.

Having found that white vitriol, mixed with snow, produced a cold of 20° , melting the snow remarkably fast, I was induced to try the freezing point of its solutions. But though it dissolved very readily in water, yet the liquor it formed was so turbid and thick, that little satisfaction could be derived from the experiments. The only numbers to be relied upon are the following, which agree sufficiently with the general result.

White vitriol.

Proportion of water to the salt.	Freezing point by the experiment.	Freezing point by calculation.	The third column is calculated from the last experiment, in which the freezing point of a solution of one part of the white vitriol in three of water proved to be $28^{\circ}\frac{2}{3}$.
10 : 1	31°	31°	
5 : 1	$29\frac{1}{2}$	30°	
3 : 1	$28\frac{2}{3}$	$28\frac{2}{3}$	

These solutions cooled very ill, none of them having sunk much below the freezing point, and the strongest, which had a copious sediment, forming a crust of ice at the bottom of the tumbler, before it was reduced at all below the term of congelation.

M. ACHARD, of Berlin, having alledged*, that borax instead of raising the boiling point of water, like other saline substances, very sensibly depresses it, I determined, however extraordinary the fact might appear, to try whether it had

* See CRELL's Chem. Annalen, 1786, Vol I. p. 501.

any peculiar effect on the freezing point. But having made the experiment with nearly a saturated solution of borax, the thermometer when it congealed was evidently below 32° : I believe about a degree.

As a neutral or middle salt, which when crystallized is always nearly of the same nature, and dissolves in a regular proportion in water, seemed likely to afford the most simple case of the effect of extraneous admixtures, it was with such that I began these experiments. But having found that with them the simple ratio prevailed, I proceeded to try substances of a more variable nature, and capable of being mixed with water in almost any proportion; such as acids, alkalies, and ardent spirits. A material difference in the law, which seemed to occur in these new experiments, renders it proper to defer the account of them till some reflections on the preceding facts, with a few additional experiments to which they gave rise, have been premised.

It is now, I believe, universally allowed, that in frigorific mixtures the melting of the snow or ice is the principal cause of the cold produced; all that heat which must become latent in order to give water its fluid form being taken from the sensible heat of the ingredients. But as, when crystallized salts are employed for the purpose, these also are reduced to a liquid form, there must, from this circumstance, be some additional cold produced, such for instance as would be occasioned by dissolving the same salt in water. Suppose then that the latent heat of water is 150 degrees, and that salt ammoniac, in dissolving to saturation, produces so much cold as sinks the whole solution about 20° ; it is evident, that if this salt and ice are mixed together in such proportions as just to melt one another, the total cold generated in the operation must amount to 170 degrees.

And so much actually is produced before the whole liquefaction is effected; and yet a mixture of these two substances will sink the thermometer no lower than to 4° of FAHRENHEIT's scale. The consideration of this apparent difficulty has led to the supposition, that a certain quantity of *fire* is contained in the crystals of the salt, which being disengaged in the solution keeps up the mixture to a certain temperature*. But I conceive, that the phænomenon depends simply on the gradual liquefaction of the ingredients, a necessary consequence of the cold produced. A saturated solution of sal ammoniac freezes itself at 4° ; therefore, when the mixture is reduced, by the liquefaction of the ingredients, to that temperature, no more of them can melt, because any addition of cold would freeze what is already melted; and if the mixture, under such circumstances, were placed in an atmosphere of its own temperature, the ingredients would remain for ever in that same state, without any further liquefaction. But in an atmosphere warmer than 4° , they continue to melt, more or less slowly, as the heat which is gradually communicated furnishes what is necessary to become latent. This communicated sensible heat being immediately converted into latent, the mixture will always be kept down to the same temperature as long as there is a sufficient mass of unmelted materials; and it can sink no lower, because then the liquefaction would be stopped; consequently such mixtures must preserve, as they have been found to do, a pretty uniform temperature, so as to have been formerly used for graduating thermometers. And the whole cold produced, or, to speak properly, the whole of the heat made to disappear, I presume to be ultimately equal to the full quantity of latent heat belonging to the dissolved ice and salt.

* DE LUC's Idées sur la Météorologie, Tom. I. p. 201.

According

According to this explanation, the greatest cold to be produced with any salt and ice or snow should be that with which a saturated solution of the same salt freezes; which was formerly established by M. DE Luc as a fact, and is in general conformable to the preceding experiments. Thus, when a solution of one part of sal ammoniac in four parts of water was put into the frigorific mixture, some of the salt was deposited, and then the solution on freezing raised the thermometer to 4° , which is exactly the cold produced by a mixture of the same salt with snow. Likewise the stronger solutions of nitre had their freezing point between 26° and 27° ; those of green vitriol near 28° ; and so of most of the other salts, corresponding with the cold of their frigorific mixtures. This agreement, however, is liable to be modified by several circumstances. For instance, if the salt be of that nature that more of it is held in solution in warm than in cold water, it becomes extremely difficult to have the solution, at the moment it freezes, exactly loaded with that quantity of salt which is most advantageous for acting upon the ice or snow. Too much may have been deposited by the cooling previous to the congelation; or some resistance having occurred to the crystallization of the salt, more of it may be retained at the moment of congelation than properly belongs to the solution at that temperature. The purity of the salts likewise, their particular nature as inclined to deliquesce or to fall down in powder in the air, the rapidity of their action upon the ice or snow, must necessarily be taken into the account, as influencing the degree of cold they can produce.

It is an evident corollary from the above-mentioned agreement, that if the freezing point of the solution of a salt in water in any known proportion be given, its degree of solubility

lity may in general be ascertained, merely by trying the greatest cold it will produce with snow.

Notwithstanding this usual correspondence between the greatest quantity of a salt that could be dissolved, and the greatest degree of cold it would produce, compared with the freezing point of its solution, I saw reason to believe that, with some salts at least, an irregularity took place in this respect. The Rochelle salt, mixed with snow, did not sink the thermometer lower than 24° ; yet the freezing point of a solution of one part of it in two of water appears, by the numbers in the table, to have been 21° . It is remarkable, however, that in the experiment with a still stronger solution, where some of the salt was deposited, the freezing point came down to 24° . Likewise the solution of white vitriol, whose freezing point was $28^{\circ}\frac{1}{2}$, deposited a copious sediment, and yet produced with snow a cold of 20° . This sediment did not look like crystallized salt, but gave a turbid appearance to the whole solution. The most remarkable circumstance of this nature, I think, occurred with the purified common salt; which, when mixed with snow, sunk the thermometer only to -4° . By experiment I found that one part of this salt would dissolve in about $2^{\circ}\frac{1}{2}$ of water. Now, if the proportions of 1 to 4 give the freezing point at $+4^{\circ}$, as by the table; 1 to $2\frac{1}{2}$ would, upon the general analogy, give it between -12° and -13° ; that is, 8 or 9 degrees lower than the greatest cold the salt would produce with snow. This circumstance leads to a suspicion, that however uniform the preceding tables appear, yet in reality something of a decreasing ratio exists, and that each subsequent addition of a salt does not depress the freezing point quite so much as the preceding. In those salts where the whole quantity of depression is but small, and in the upper

part

part of the scale in those which have a greater effect, this progression may be insensible, or be incapable of determination by such experiments as these, which by their nature do not admit of extreme accuracy; but it may become sufficiently observable toward the last additions of such salts as are soluble in great quantity, and such as alter very much the freezing point. I never succeeded to freeze the saturated solution of this Borrowstounnes common salt, though it has been cooled several degrees below -4° without depositing any of its salt; if the experiment were made in a cold sufficient for the purpose, it would shew whether any irregularity takes place in the action of this salt upon snow, or whether such a decreasing ratio does exist. Perhaps, however, the whole may depend upon the principle alluded to formerly, that the presence of some salt favours the deposition of more: for when a salt is mixed with snow, it may in this point of view be considered as in the same state with a saturated solution of the salt which has some of it remaining undissolved; and which, therefore, will not contain more than properly belongs to it at the given temperature; and the cold of such a frigorific mixture should be no greater than that of the freezing point of the saturated solution under those circumstances.

As it is well known that water, after it has been saturated with one salt, will take up a certain portion of another salt without depositing any of the former, I was curious to try what effect the addition of this second salt would produce on the freezing point; and particularly whether it would depress the freezing point of the saturated solution the same number of degrees that an equal proportion of the same salt would depress the freezing point of water; and whether the same simple

simple ratio would hold good, or any new law take place. To bring this to the test of experiment, I took a saturated solution of nitre, whose freezing point of course was between 26° and 27° : and adding to it the purified common salt in various proportions, I obtained the following results.

Compound solution of nitre and common salt.

Proportion of water to the nitre.	Proportion of water to the common salt.	Freezing point by the experiment.	Freezing point by calculation.	Difference.
A saturated solution.	30, 2 : 1	$23\frac{1}{2}$	$22\frac{3}{4}$	$\frac{1}{4}$
	15 : 1	$20\frac{3}{4}$	19	$1\frac{3}{4}$
	10 : 1	$17\frac{1}{2}$	$15\frac{1}{4}$	$2\frac{1}{4}$
	7, 4 : 1	$13\frac{1}{2}$	$11\frac{1}{2}$	2
	5 : 1	$5\frac{1}{4}$	4	$1\frac{1}{4}$

The solution of nitre was one that had been made some time, and contained near one-sixth part of nitre, consequently more than the water could keep dissolved in the temperature of the atmosphere, which was then not much above 40° . Some of it therefore was deposited at the bottom. This, however, the addition of a $\frac{1}{32}$ part of common salt soon enabled the water to take up, and the two salts formed together a clear solution. In the frigorific mixture, before the congelation took place, some saline crystals were again deposited, which seemed to be chiefly, if not entirely, nitre. In the temperature of the air this deposit was re-dissolved; and on attending to the circumstances more carefully, upon a repetition of the cooling, I found, that no salt began to be deposited till the solution was reduced to 23° , when some needle-like crystals appeared, which consequently were nitre. The solution cooled about a degree more, and then, having let fall much salt, partly as crystals

and partly, by stirring, as a powder, it was made to congeal by dropping in a bit of snow, and the thermometer rose to $23^{\circ}\frac{1}{2}$. When more salt was added, to render its proportion to the water as 1 : 15, the nitre seemed still more difficultly deposited in the freezing mixture; and this continued to be the effect of further additions of salt, the deposition of saline matter previous to the congelation being always less, in proportion as the quantity of common salt was greater.

It is evident from the freezing points of this compound solution, that the common salt depressed the freezing point of the solution of nitre something less than it would have depressed the freezing point of water, if added to it in the same proportion. To shew this more evidently, I have added a fourth and a fifth column to the table: the fourth column is formed by taking the freezing point of the saturated solution of nitre as $26^{\circ}\frac{1}{2}$, and then finding how many degrees the quantity of common salt added would have depressed the freezing point of water; this number of degrees, subtracted from the constant number $26^{\circ}\frac{1}{2}$, gives the freezing point by calculation; namely, what it should have been if the salt had produced the same effect upon the solution of nitre as it would upon pure water; and the difference between this and the freezing point found by the experiment gives the numbers in the fifth column. From the table it is apparent, that the deficiency of effect from the salt goes on increasing to the third experiment, after which it decreases. Probably some particular law takes place, which it would require a great number of experiments to develope; but the decrease toward the last may in part be owing to the greater quantity of nitre which the water, when it began to be loaded with common salt, retained at the time of congelation, and which must have its effect in depressing

depressing the freezing point. The above-mentioned circumstance seems rather contradictory to an opinion which has been entertained, that when one salt, added to a saturated solution of another salt, enables it to take up more of the former salt, it is only because the water of crystallization of the second salt really adds to the quantity of the dissolving fluid.

I next proceeded to try a similar experiment with sal ammoniac and the purified common salt, but with this difference, that neither salt should be added to the water in such quantity as to come near the point of saturation, suspecting that the diminution of effect observed in the foregoing experiments might depend, in part at least, upon this circumstance. The sal ammoniac, therefore, was dissolved in water in the proportion of 1 : 10, and the corresponding point of congelation appeared by experiment to be $20^{\circ}\frac{1}{2}$, agreeing very well with the table of sal ammoniac formerly given. To this solution was added the purified common salt, in proportion to the water as 1 : 15, and then as 1 : 10; the resulting points of congelation were as is shewn in the following table, constructed in all respects as the immediately preceding.

Compound solution of sal ammoniac and common salt.

Proportion of water to the sal ammoniac.	Proportion of water to the common salt.	Freezing point by the experiment.	Freezing point by calculation.	Difference.
10 : 1	15 : 1	$12\frac{3}{4}$	13°	$+\frac{1}{4}$
10 : 1	10 : 1	$9\frac{1}{4}$	$9\frac{1}{5}$	$-\frac{1}{20}$

Hence it appears, that in this compound solution both salts produced, as exactly as the experiments can be expected to shew,

shew, their full effect in depressing the point of congelation. When the solutions at length froze, after cooling many degrees below the freezing point, the crystals shot in a very beautiful manner round the bulb and up the stem of the thermometer.

In a compound solution of Rochelle and common salt there was, however, a deficiency of effect. For the solution of Rochelle salt in the proportion of one part to four of water, having its freezing point at $26^{\circ}\frac{1}{3}$; when common salt was dissolved in it, in the proportion of $\frac{1}{4}$ th, the freezing point appeared by experiment to be $16^{\circ}\frac{1}{4}$, whereas by calculation it should have been depressed nearly to 15° .

A composition of three salts was affected as follows :

Compound solution of Rochelle salt, common salt, and salt ammoniac.

Proportion of water to the Rochelle salt.	Proportion of water to the common salt.	Proportion of water to the salt ammoniac.	Freezing point by the experiment.	Freezing point by calculation.	Difference.
9,8 : 1	10 : 1	17 : 1	13° -	$11\frac{1}{2}^{\circ}$	$-1\frac{1}{2}^{\circ}$

The computation is made thus : Rochelle salt, in the proportion of $1 : 9,8$, depresses the freezing point $2^{\circ}\frac{1}{4}$; common salt, in the proportion of $1 : 10$, sinks it $11^{\circ}\frac{1}{4}$; and salt ammoniac, in the proportion of $1 : 17$, sinks it 7° ; now $2\frac{1}{4} + 11\frac{1}{4} + 7 = 20\frac{1}{2}$; which, subtracted from 32, leaves $11\frac{1}{2}$ for the computed freezing point of this mixture.

The moment I had found by experiment that the addition of a different salt to the saturated solution of any salt would still further depress its freezing point, it was obvious to con-

clude, that greater cold could be produced with snow by a mixture of salts than by means of either taken separately. I made several experiments with this view, and found it uniformly the fact, that by adding a certain proportion of a salt which had less power of producing cold with snow, to one which had a greater power, the frigorific effect of the latter was sensibly increased. Passing over examples of less consequence, it will be sufficient to instance common salt and salt ammoniac. The ordinary common salt I used to mix with snow, sunk the thermometer to -5° ; the salt ammoniac to $+4^{\circ}$; but when some of the latter salt was mixed with the former, the composition produced with snow a cold of -12° . I did not carry the experiments far enough to determine the proportions which answered best, but saw evidently, that a considerable variety in this respect occasioned scarcely a perceptible difference: more salt ammoniac was, however, required, than that proportion of it to the common salt, which ought, by computation, to have sunk a saturated solution of the latter 7 degrees. On several occasions I made use of this composition to obtain a greater degree of cold than common salt alone would produce, and found it a very convenient method.

On this principle it is that impure common salt always makes a stronger freezing mixture than the pure; it being, in fact, a composition of salts. I have seen three salts produce a greater cold than two, but have not carried the experiments far enough to ascertain the limits of this effect *.

M.

* The curious experiments, related in the Philosophical Transactions for 1787, p. 282. of producing a great degree of cold by dissolving a mixture of salts in water, depend in part upon the same principle, the water being capable of reducing more salt from a solid to a fluid state when several kinds are employed.

M. DE REAUMUR proposed to try what cold gunpowder would produce with snow, as a test of its goodness, that is, of the purity of the nitre in its composition. It is evident, from what has been delivered above, that if any saline impurity be mixed with the nitre, a frigorific mixture formed with the composition will be lower than $26^{\circ}\frac{1}{2}$, a greater or less number of degrees, according to the nature and quantity of the impurity; and if it be only common salt, the proportion of it to the nitre may be thus determined pretty nearly.

As the cold produced by common salt with snow is -4° or more, and by sal ammoniac $+4^{\circ}$, it is difficult to conceive in what manner FAHRENHEIT fixed the zero of his thermometer. All those who have examined the few authentic passages to be found in authors upon this subject, will be sensible how vaguely they are expressed, leaving it doubtful whether he used common salt alone, sal ammoniac alone, or both mixed together. There is no method of sinking a thermometer exactly to 0° with these salts and snow, but by means of a certain smaller proportion of common salt added to the sal ammoniac; and it would have been an extraordinary chance, that FAHRENHEIT should hit precisely this proportion often enough to make him rely upon the point so found as the commencement of his scale; more especially as the proportion

employed, than it could of one of the kinds only. A remarkable fact of this nature, as I imagine, is recorded so early as in the Memoirs of the French Academy of Sciences for 1700, p. 116. "On prend une livre de sublimé corrosif, et une "livre de sel ammoniac; on les pulvérise chacun à part; on mêle ensuite les "deux poudres très exactement; on met le mélange dans un matras, versant "par-dessus trois chopines de vinaigre distillé; on agite bien le tout: et ce me- "lange se refroidit si fort, qu'on a peine à tenir long-tems le vaisseau dans les "mains en été. Il est arrivé même quelque fois à M. HOMBERG, que faisant ce "mélange en grande quantité, la matière s'est gelé."

is probably no greater than a seventh or a sixth of common salt to the sal ammoniac. Is it possible that FAHRENHEIT, finding a considerable difference in his experiments, took the mean between them for his zero, without any respect to the different nature of the salts with which he operated? It appears, that he was at this time so little acquainted with the subject, as to consider his zero as the utmost limit of cold.

I come now to certain substances which, by equal additions, seem to depress the freezing point of water in an *increasing ratio*. These, as was mentioned before, are acids, alkalies, and spirit of wine. I judge this to be the case from the following experiments, though they are by no means so full and extensive as I could have wished to make them, had leisure permitted.

The specific gravity of the vitriolic acid I employed was 1,837 at 62° of heat; its effect upon the freezing point is shewn by the following table.

Vitriolic acid.

Proportion of water to acid.	Freezing point by the experiment.	Freezing point by calculation.
10 : 1	24 $\frac{1}{2}$	22 $\frac{1}{4}$
5 : 1	12 $\frac{1}{2}$	12 $\frac{2}{5}$
4 : 1	7 $\frac{1}{2}$	7 $\frac{1}{2}$

This table is constructed in the same manner as those formerly given of the solution of simple salts; the last experiment, where the proportion is 4 : 1, being taken as the standard for computation; and the extreme difference between the calculation and experiment is no less than 2° $\frac{1}{4}$, upon a reduction

reduction of the freezing point from $24^{\circ}\frac{1}{2}$ to $7^{\circ}\frac{1}{2}$. The freezing point, set down in the table, is that to which the liquor rose upon congealing, after having been cooled several degrees lower; which it is proper to remark, because the ice rose two or three degrees in thawing.

The nitrous acid I employed was smoking, and had its specific gravity 1,454. It acted on the freezing point according to the following table, which is constructed in all respects like the preceding.

Proportion of water to acid.	Freezing point by experiment.	Freezing point by calculation.
16,8 : 1	$26\frac{1}{3}$	$25\frac{2}{3}$
10 : 1	$22 -$	$21\frac{1}{2}$
7,64 : 1	18	18
5,06 : 1	$10\frac{1}{2}$	11
4,26 : 1	7	7

The greatest difference between the calculation and experiment appears here to be only two-thirds of a degree; but that is more than, I think, can be attributed to inaccuracy. These mixtures cooled remarkably well; that in which the water was to the acid as 7,64 : 1 sunk down to 6° before it froze. The ice heated about a degree before it was melted.

Spirit of salt being a very weak acid, its increase of ratio was not perceptible within the limits to which I was confined.

Muriatic acid.

Proportion of water to acid.	Freezing point by experiment.	Freezing point by calculation.
10 : 1	25°	25°
5,1 : 1	18 $\frac{4}{5}$	18 $\frac{1}{2}$
3,05 : 1	9 $\frac{1}{3}$	9 $\frac{1}{3}$

This table is constructed as the foregoing; and the specific gravity of the marine acid was 1,163.

Salt of tartar, such as is usually sold in the shops, was the vegetable alkali I employed. It did not readily deliquesce, and consequently was not very caustic: the cold it produced with snow was - 12°.

Salt of tartar.

Proportion of water to alkali.	Freezing point by experiment.	Freezing point by calculation.
10 : 1	27 $\frac{1}{4}$	26 $\frac{1}{2}$
7,5 : 1	25 $\frac{1}{2}$	24 $\frac{4}{5}$
5 : 1	22 $\frac{3}{4}$	21 $\frac{1}{3}$
3 : 1	15	14
2,5 : 1	11 $\frac{3}{4}$	10 $\frac{1}{2}$
2 : 1	5	5

Here the greatest difference between the calculation and experiment is something more than 1 $\frac{1}{2}$ degree, in sinking the freezing point from 22° $\frac{3}{4}$ to 5°; but in the higher freezing points of the table it is less, as well as in the lower. Perhaps

this irregularity in the experiments is in part to be ascribed to an impurity in the salt of tartar; a turbid appearance, and at length a deposition, took place in all these solutions, but principally in the stronger, occasioned probably by tartar of vitriol, with which that salt is so frequently mixed.

The mineral alkali I tried, which was the crystallized soda of the shops, shewed no increase of ratio; but the scale of its operation was too small for a proper judgement to be formed.

Mineral Alkali.

Proportion of water to alkali.	Freezing point by experiment.	Freezing point by calculation.
10 : 1	30° -	29 $\frac{9}{10}$ °
5 : 1	27 $\frac{4}{5}$	27 $\frac{4}{5}$

This salt would not remain suspended in much greater proportion in the cooled water. I consider the solutions as decreasing in their freezing point by an equal ratio: possibly, if the salt of tartar had been crystallized, and perfectly saturated with fixed air, it would also have acted in the manner of a neutral salt, and produced no increase upon the ratio.

■ My volatile alkali, being the sal volatilis salis ammoniaci, was tried only in two proportions.

Volatile alkali.

Proportion of water to alkali.	Freezing point by experiment.	Freezing point by calculation.
10 : 1	25°	25 $\frac{1}{4}$ °
5,18 : 1	19	19

Here also there is no appearance of an increase of ratio, but rather the contrary.

The specific gravity of the spirit of wine I employed was ,829 at 62°. It depressed the freezing point according to the following table.

Spirit of wine.

Proportion of water to spirit.	Freezing point by experiment.	Freezing point by calculation.
8,5 : 1	24 $\frac{1}{2}$	23 $\frac{3}{4}$
5 : 1	17	18
3,66 : 1	12 $\frac{1}{4}$	12 $\frac{3}{4}$
3 : 1	8 $\frac{1}{2}$	8 $\frac{2}{3}$
2,5 : 1	4	4

The total difference between the calculation and experiment, upon a reduction of the freezing point from 24 $\frac{1}{2}$ to 4°, is $\frac{3}{4}$ of a degree; but the intermediate points are very irregular, and in an opposite sense, as if the ratio were decreasing. It seems more probable, that some inaccuracy in the experiments, perhaps owing in part to the evaporation of the spirits, should be

the occasion of this, than that there should be such an irregularity in the law.

If any person should alledge, that the difference between the observed and computed freezing points in the foregoing tables is not sufficient to establish the increase of ratio, I can only reply, that it appears to me greater than can reasonably be ascribed to error in the experiment; especially as similar experiments with neutral salts, not conducted more attentively, agreed so well together in pointing out a different law. It must be allowed, however, that the experiments do not shew any increase of ratio, except in the vitriolic and nitrous acids, salt of tartar, and, with more ambiguity, in spirit of wine: from analogy only I suspect it to take place in the other acids, and in the mineral and volatile alkalies provided they are caustic. That a different law from what prevails in the neutral salts should take place with these substances, seems not surprising, when it is considered how much stronger attraction they shew for water, and how much less limited the proportion is in which they will unite to it: for the same reasons, I should not think it extraordinary, if deliquescent salts, combined with water, should be found to observe the same increasing ratio in depressing the freezing point.

As other experiments upon the watery congelation of acids, and in lower degrees of cold, have been given to the public, it would have been desirable to compare them with mine, and thus to have obtained a greater length of scale. But the difficulty of ascertaining the precise strength of different acids is so great, and a small uncertainty in this respect may occasion so much error, that I conceive little reliance can be placed, with regard to the present object, upon any experiments except such as are

made by diluting the *same* acid with different proportions of water.

I shall conclude this Paper with the account of an experiment to determine the effect of salt upon the expansion of water by cold. Pure water begins to shew this expansion about the temperature of 40° , that is, 8 degrees above its freezing point. I put a solution of common salt, in the proportions of 4,8 parts of water to one of the salt, and consequently whose freezing point was $8^{\circ}\frac{2}{3}$, into an apparatus I had used for other experiments of the same kind; and found that the solution continued to contract till it was cooled to 17° , but had sensibly expanded by the time it was cooled to 15° . Suppose the expansion to have begun at $16^{\circ}\frac{2}{3}$, it would be just 8 degrees above its new freezing point. Hence we have reason to conclude, as far as one experiment goes, that the combination of a salt with water has no other effect upon its quality of expanding by cold, than to depress the point at which that quality begins to be sensible, just as much as it depresses the point of congelation.

It is probable, that the subject of this Paper will appear to some minute and trifling. Did it lead to nothing further, that opinion might be just. But it is by the accumulation of facts of this kind, and especially such as have been developed by Mr. CAVENDISH in his excellent Papers on the freezing of acids *, that the foundation must be laid for a general theory of the laws of cohesion, which may ultimately lead to a knowledge of the structure upon which the intimate properties of

* Philosophical Transactions, Vol. LXXVI. p. 241. and p. 166. of this Volume.

bodies depend; in the same manner as more accurate observations of the different motions of the great masses in the universe, paved the way to the sublime discoveries of KEPLER and NEWTON.

